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(54) Title: CATALYTICALLY POLYMERIZED FIBER-REINFORCED COMPOSITES

(57) Abstract: A sizing that is highly compatible with catalysts used in the ring opening metathesis polymerization of cycloolefins is disclosed. The sizing includes a specific combination of ingredients that, when applied to reinforcing fibers used in the manufacture of composites, enables molding of the fibers with catalyzed cycloolefin resin without poisoning of the catalyst. Also disclosed is a method of manufacturing fiber-reinforced composites using fiber products comprising the sizing of the invention.

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## CATALYTICALLY POLYMERIZED FIBER-REINFORCED COMPOSITES

## TECHNICAL FIELD AND INDUSTRIAL

APPLICABILITY OF THE INVENTION

5           The present invention relates to a sizing composition for coating glass or other fibers that are used to manufacture fiber-reinforced composites using a cycloolefin resin. The composition is advantageously compatible with the catalyst, in that chemical interactions between the catalyst and the components of the sizing are eliminated.

10

BACKGROUND OF THE INVENTION

          Due to their corrosion resistance, light weight, design flexibility and efficiency, and cost effectiveness, fiber-reinforced composites are finding ever increasing use in industries such as the aerospace, automotive, chemical and oil, electronic, infrastructure, and military industries. The reinforcements for these composites may initially be formed as fabrics, mats, pellets, chopped strands, or unidirectional fiber products such as rovings or strands. These intermediate products may be further processed and combined with various matrices to form useful articles such as engine cowlings, grill opening panels, pipes, circuit boards, structural beams, missile launch tubes, and other molded products.

20   The molded products typically comprise a fiber-reinforcement component and a molding resin, and may further include fillers, pigments, catalysts and other processing aids. The fiber reinforcements are typically coated with a protective sizing that provides resilience to the fibers and aids in the processing and wettability of the fibers in the molding resin. The sizings themselves may comprise thermoplastic or thermosetting resins, and may

25   include components known to enhance coating ability and reduce abrasion between fibers and contact points. It is desirable that the sizing used to coat the glass be highly compatible with the molding resin that forms the rest of the composite product.

          Impregnating or molding resins for producing composites include, for example, polyesters, vinylesters, epoxies, phenolics, polyurethanes, polyimides, bismaleimides, polycarbonates, nylons, polyether-etherketones, polyphenylene sulfides, polyetherimides, polyvinylchlorides, polystyrenes, polyethylenes, polypropylenes, or other polyolefins. Of

30   particular interest to this invention are cycloolefins, which can be polymerized by a ring opening metathesis polymerization reaction (ROMP). The cycloolefins usually must be

polymerized in the presence of a ROMP catalyst to solidify the composite. Such ROMP catalysts include tungsten and molybdenum compounds, such as those disclosed in U.S. Patent Nos. 4,427,595, 4,681, 956, 4,727,215, 4,882,401 and 5,082,909. Typically, these ROMP catalysts have been used in combination with aluminum alkoxy compounds or alkylaluminum compounds as co-catalysts. In addition to being time-consuming, the use of the aluminum co-catalysts is often detrimental to the polymerization process, because the presence of even slight amounts of water inhibits their activity. Since small amounts of water are normally present on the surfaces of glass fibers after forming, the effectiveness of the polymerization process is often compromised, and the resulting product, instead of being a tough, hard composite material, has an undesirable, soft, rubbery consistency.

Recently, efforts to find an improved ROMP catalyst for polymerization of cycloolefins have resulted in the development of ruthenium or osmium carbene compounds, which have proven to be highly effective at initiating ROMP polymerization of cycloolefins. Such catalysts are described, for example, in U.S. Patent Nos. 5,312,940, 5,342,909, 5,831,108, 5,849,851 and 5,939,504. These catalysts demonstrate a high level of metathesis activity in contrast to previous non-carbene ruthenium and osmium compounds, which were limited by their ability to catalyze only sterically strained cycloolefins. Further, these ruthenium and osmium catalysts do not require the additional use of the above discussed aluminum co-catalyst compounds, and thus these catalysts do not suffer from the same intolerance to moisture. However, a significant drawback of using these ruthenium and osmium carbene catalysts in the polymerization of typical composite formulations containing cycloolefin resins such as dicyclopentadiene (DCPD), is that the ingredients typically used to prepare the fiber reinforcement material poison these carbene catalysts, thereby reducing or eliminating their effectiveness. The term "poison", as it is used herein with respect to the ingredients used to prepare fiber reinforcement materials, is intended to mean that these ingredients inhibit, slow, prevent or terminate the desired polymerization reaction. For example, the components of conventional sizing formulations, such as polymers, lubricants and other additives are poisonous to the osmium and ruthenium carbene catalysts and therefore hinder the catalytic reaction needed to cure the resin. The result is that the end product is soft and rubbery, instead of being a hardened and resilient composite. This incompatibility between the sizing and the catalyst is a significant problem in the art, which, heretofore,

has not been addressed.

There is, therefore, a need in the art for a sizing composition for reinforcing fibers that is compatible with ROMP catalysts used to cure cycloolefin resins. It is desirable that such a sizing composition should also result in low fuzz development in the forming and subsequent processing of the packages of formed reinforcing fibers.

#### SUMMARY OF THE INVENTION

The present invention relates to an improved sizing composition for reinforcing fiber materials that is compatible with catalysts used to initiate a ring opening metathesis (ROMP) polymerization of a cycloolefin resin, this sizing composition comprising:

- one or more film forming polymers;
- a silane coupling agent; and
- a lubricant;

wherein the film forming polymer, the silane coupling agent and the lubricant are compatible with one or more ROMP catalysts used to initiate ring opening metathesis polymerization of the cycloolefin resins.

The invention also relates to a method of making a sized reinforcing fiber material comprising the steps of:

- i) preparing a sizing composition comprising:
  - one or more film forming polymers;
  - a silane coupling agent; and
  - a lubricant;wherein the film forming polymer, the silane coupling agent and the lubricant are compatible with one or more ROMP catalysts used to initiate ring opening metathesis polymerization of the cycloolefin resins ;
- ii) contacting the surfaces of a plurality of filaments of a reinforcing fiber material with the sizing composition; and
- iii) allowing the sizing composition to solidify onto the surfaces of the filaments of the reinforcing fiber material.

The invention also relates to a sized reinforcing fiber material coated with the sizing composition of the present invention.

The present invention further relates to a molded composite article comprising (i) a reinforcing fiber material sized with the sizing composition of the present invention, and (ii) a cycloolefin resin polymerized using a ROMP catalyst.

5 The present invention additionally includes a method of making a fiber reinforced composite, comprising the steps of:

- (i) applying a sizing composition on the surfaces of a reinforcing fiber material, the sizing composition comprising:
  - one or more film forming polymers
  - a silane coupling agent; and
  - 10 a lubricant;to form a coated reinforcing fiber material; and
- (ii) molding the coated reinforcing fiber material with a cycloolefin resin in the presence of a ROMP catalyst to form a fiber reinforced composite;

15 wherein the film forming polymer, the silane coupling agent and the lubricant in the sizing composition are compatible with one or more ROMP catalysts used to initiate ring opening metathesis polymerization of the cycloolefin resins.

The invention additionally comprises a composite article comprising a sized reinforcing fiber material coated with the sizing composition comprising a film forming polymer, a silane coupling agent and a lubricant; wherein the film forming polymer,  
20 silane coupling agent lubricant are compatible ROMP catalysts used to initiate ring opening metathesis polymerization of cycloolefin resins.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

25 The present invention relates to a sizing composition that is highly compatible with ROMP catalysts used in the ring opening metathesis polymerization of cycloolefins. The term "compatible", as used herein, is intended to mean that the sizing does not poison the catalyst or interact, in any other way, so as to diminish the effectiveness of the catalyst when it is added to the cycloolefin resin. Moreover, the sizing composition, when applied  
30 to reinforcing fiber materials used in composite winding, molding or casting, provides desirable properties such as good compatibility with a molding resin, reduced fuzz and good shear strength. Sizing compositions previously known in the art lacked such compatibility with ROMP catalysts, either because the catalysts or required co-catalysts

were sensitive to water present on the surface of the reinforcing fiber component; or because the ingredients of these sizing compositions suppressed the activity of the ROMP catalysts. While the reason for the effectiveness of the sizing compositions of the present invention has not been definitively established, the inventors believe that it may be due, in part, to the absence of ionic species, such as salt impurities, in the sizing composition. It is believed that these ionic species, if present, could interact with the ROMP catalyst, to deactivate it. It is further believed that the effectiveness of the sizing compositions of this invention may also be attributed to the absence of certain reactive functional groups on the molecules of the various ingredients of the sizing composition. As a result of the absence of these reactive functional groups, it is believed that the molecules of the various ingredients of the sizing composition cannot react with the catalyst and therefore cannot cause a poisoning effect. In contrast, the conventional sizings of the prior art contain ionic species, such as salt or certain nucleophilic impurities, which appear to interact adversely with the ROMP catalyst.

The sizing composition of the present invention may include one or more film forming polymers selected from the group consisting of film forming polymers compatible with the ROMP catalyst used to initiate ring opening metathesis polymerization of cycloolefin resins. The film forming polymer improves the wettability of the sizing and protects the individual fibers and fiber bundles within the reinforcing fiber material during processing by providing a controlled level of strand integrity, which is the ability of the fibers to adhere together during processing. Suitable film forming polymers may be selected from the group consisting of bis-A epichlorohydrin epoxies, modified epoxies, epoxy-polyesters, epoxy-polyurethanes, epoxy novolac resins, polyvinyl acetates, vinylacrylics, styrenated acrylics, polybutylacrylates, saturated or unsaturated polyesters, polyurethanes, polyamides, paraffin waxes, carnauba waxes, micro-crystalline waxes, polyethylenes, polypropylenes, polycarboxylic acids, polyvinyl alcohols and mixtures thereof. Examples of preferred film forming polymers are: a polyurethane such as "Witcobond 320", which is available commercially as a liquid emulsion from Witco Inc; an acrylic resin such as "NS-7170", which is commercially available from National Starch Inc.; and a styrenated acrylic resin such as "Product No. 3661", which is commercially available from H.B. Fuller Inc. Typically, the amount of the film former in the aqueous size mixture ranges from about 0.5% by weight to about 10.0% by weight. Preferably, the amount used is from about 3% by weight to about 5%

by weight.

The sizing composition of the present invention also includes a silane coupling agent, which is compatible with ROMP catalysts. The silane coupling agent improves the adhesion between the sized fiber surface and the composite matrix resin, by providing functional groups for reaction with the surface molecules of the fiber and the matrix resin, in effect acting as a "bridge" between the inorganic fiber surface and the organic composite matrix resin. Suitable silane coupling agents include ROMP-compatible silanes, such as those commercially available from OSi, Inc., a division of Witco, and Dow Corning, Inc. Examples of these include: vinyltrimethoxysilane, commercially available under the tradename "A-171" from OSi, Inc., or as "Q 96300" from Dow Corning Inc.; vinyltriethoxysilane, commercially available under the tradename "A-151" from OSi, Inc.; phenylaminosilane, commercially available under the tradename "9669" from OSi, Inc.; methacryloxypropyltriethoxysilane, commercially available under the tradename "A-174" from OSi, Inc.; n-2-(vinylbenzylaminoo)-ethyl-3-aminopropyltrimethoxysilane-monohydrogen chloride, commercially available under the tradename "Z-6032" from Dow Corning; and gamma aminopropyltriethoxysilane, commercially available under the tradename "A-1100" from OSi, Inc. One preferred ROMP compatible silane is vinyltrimethoxysilane. Preferably, the silane coupling agent is used in an amount of from about 0.3% to about 1.0% by weight based upon the total weight of the sizing composition. At concentrations above 1.0%, the resulting product is of undesirable quality because the silane increases fuzz development. Therefore, it is necessary to balance the amount of the silane sufficiently to provide the desired coupling effect, but without promoting high levels of fuzz in the sized product.

Preferably, the sizing composition also includes a cationic lubricant that is compatible with the ROMP catalysts. The cationic lubricant is added to the sizing to reduce the development of fuzz and to improve the coating ability of the sizing composition. The cationic lubricant may be selected from the group consisting of functionalized polyalkyleneimines. Examples of suitable cationic lubricants include water-soluble, partially amidated polyethyleneimines (PEIs) substituted with a varying number of ethylene residues, for example PEI-12. One example of a cationic lubricant based on PEI-12 is a cationic lubricant, "Henkel 6760T", which is commercially available from Henkel, Inc. Other exemplary cationic lubricants include fatty acid amine cationic lubricants such as a cocoamine acetate, available as "PF-710" from Henkel Inc.; or the

reaction products of tetraethylene pentamine with stearic acid, pelargonic, or caprylic acid. Preferably, the cationic lubricant is used in an amount of from about 0.04% to about 0.25% by weight based upon the total weight of the sizing composition. At an amount over 0.2% by weight, however, some discoloration of the fiber package formed from the sized reinforcing fiber material may occur. Such discoloration is an aesthetically undesirable result. More preferably, therefore, the cationic lubricant is used in an amount of from about 0.05% to about 0.1% by weight based upon the total weight of the sizing composition.

Optionally, a second lubricant, which is preferably a nonionic lubricant, may be added to the sizing composition. In one modification of the present invention, this second lubricant may be substituted for the cationic lubricant. Suitable as a second lubricant is a polyethyleneglycol monoester, for example, a polyethyleneglycol monopelargonate having the tradename "Emerstat 2658", which is a nonionic lubricant that is commercially available from Henkel, Inc. Preferably, the second lubricant, when used in combination with the cationic lubricant, may be used in an amount from about 0 to about 1.5% by weight based upon the total weight of the sizing composition, and more preferably at from 0 to about 0.5% weight.

A suitable emulsified wax may be added to the sizing composition. The term "emulsified wax", as used herein, is intended to encompass olefinic wax compounds, including polyethylenes and polypropylenes, or mixtures thereof, that have been emulsified by combination with a surfactant, which is preferably a nonionic surfactant. The addition of a surfactant to emulsify the wax serves to improve the solubility or dispersibility of the emulsified wax in the sizing composition. Suitable emulsified waxes include paraffins, carnauba and polyolefins. Preferably, the emulsified wax is an emulsified paraffin wax. The emulsified paraffin wax acts as a modifier for the one or more film forming polymers in the sizing composition, and also acts as a lubricant within the sizing composition. An example of a suitable emulsified paraffin wax is "FIBERGLASS X-12", an emulsion that is commercially available from Michelman Inc. or "Velvetrol 77-70", available commercially from Rhone Poulenc. The amount of emulsified paraffin wax in the sizing composition may range from 0 to about 5% by weight, preferably from about 1% by weight to about 4% by weight, and more preferably about 2.3% by weight, based on the total weight of the sizing composition.

A hydrolyzing agent for hydrolyzing the silane coupling agent may also be



included in the sizing composition. Any suitable hydrolyzing agent that promotes the hydrolysis of the alkoxy groups on the silane-coupling agent to hydroxyl groups may be used. Examples of suitable hydrolyzing agents include hydrochloric, acetic, formic, citric, oxalic and phosphorous acids. Preferably, an effective amount of glacial acetic acid is used as the hydrolyzing agent. Typically, an effective amount of glacial acetic acid may be from about 0.25% to about 0.5% by weight based upon the total weight of the sizing composition. More preferably, about 0.25% by weight of glacial acid, based upon the total weight of the sizing composition, is used. While the sizing composition may generally be of a pH in the range of from about 2 to about 10, it is recognized that the glacial acetic acid, or any of the other suitable hydrolyzing agents, also performs the additional function of maintaining the pH of the sizing composition in a preferred range of from about pH 3 to about pH 5.

The sizing composition may also include one or more additives useful to improve wetting, processing and the reduction of fuzz. Such agents may be selected from the group consisting of processing aids, wetting agents and other additives.

Any suitable processing aid may be used. Suitable processing aids may include one or more compounds selected from the group consisting of salt-free polyethylene glycol (hereinafter "PEG") compounds such as PEG monopelargonate and other PEG fatty acid esters, polyvinylpyrrolidones and pentaerythritols. Polyvinylpyrrolidones, for example, enhance pick-up of the sizing composition by the reinforcing fiber material by up to about 20%. The processing aid is added to facilitate contact between the sizing and the fiber surface. A particularly useful processing aid is a salt-free PEG 400 monopelargonate ester, which is highly compatible with, and which does not inhibit the cure of DCPD resin. The term "salt-free", as used herein, is intended to mean the absence of substantially any ionic species, residues or functional groups in a preparation containing the pelargonate ester. The inventors have unexpectedly discovered that this salt-free PEG 400 monopelargonate does not poison the ROMP catalysts, unlike other PEG compounds, which are traditionally used in sizing formulations. A salt-free PEG 400 monopelargonate is commercially available, for example, as "Emery 2658", from Henkel, Inc.

In a preferred embodiment of the present invention, the sizing composition comprises a film forming polymer, a silane coupling agent, a cationic lubricant and a

hydrolyzing agent. In another preferred embodiment, the sizing composition further comprises an emulsified paraffin wax that is compatible with the ROMP catalyst.

The sizing composition of the present invention may be made by any method known to one of ordinary skill in the art. For example, the sizing composition may be made by blending the individual components of the sizing composition with a diluent to form a solution or suspension. Preferably, the diluent is water. The components such as the film-forming polymer, the coupling agent, the hydrolyzing agent, the lubricants and processing aids are preferably used in amounts effective to formulate a stable dispersion having a storage stability of up to about 72 hours at temperatures from about 50°F to about 120°F, and a pH of from about 3 to about 5.

The sizing composition of the present invention may be applied to the reinforcing fiber material by any suitable method, to form a coated fiber reinforcing material. For example, the sizing composition may be applied to filaments of a reinforcing fiber material immediately after they are formed in an on-line operation, or the sizing composition may be applied, off-line, to unwound strands of reinforcing fiber material that were previously formed and packaged. The invention may also be applied to the reinforcing fiber material after it has been woven or knitted into a fabric. Means for applying the sizing composition include, but are not limited to, pads, sprayers, rollers or immersion baths. Preferably, the reinforcing fibers are wetted with the sizing composition as soon as they are formed. For example, the sizing composition may be sprayed onto continuous glass fibers as they are formed from a bushing or like device. The bushing is equipped with small apertures to allow passage of thin streams of the molten material. As the molten material emerges from the bushing apertures, each stream is attenuated and pulled downward to form a long, continuous fiber. The continuously forming fibers may be gathered into strands for winding. The forming packages or doffs formed by the above-described winding operation are then dried for about 13 to 25 hours at 265°F, after which they are ready for use in composite-making operations such as filament winding.

The amount of sizing composition that is applied to the surfaces of the reinforcing fiber material may be selected to provide an effective thickness of the sizing composition on the surfaces of the reinforcing fiber material. If an insufficient coating of the sizing composition is applied, the fibers of the reinforcing fiber material are not protected during the processing operation, which results in unnecessary fuzz development caused by broken fiber filaments in the sized reinforcing fiber material. Another effect of

insufficient coating is that the ability of the fibers of the reinforcing fiber material to wet out in a molding resin, such as the cycloolefin resin, during the composite forming process is reduced. Conversely, if too much sizing composition is applied, it becomes more difficult for the molding resin to penetrate the size and encapsulate the filaments of the reinforcing fiber material. It is therefore desirable to balance these factors during application of the sizing composition. Accordingly, the effective amount of sizing composition that should be applied to the reinforcing fiber material is determined by monitoring the loss on ignition (LOI) value, which is a measure of the amount of sizing present on the surfaces of the sized reinforcing fiber material. The amount of sizing composition deposited on the surfaces of the reinforcing fiber material, that is, the size pickup, and, inherently, the thickness of the sizing coating may then be adjusted by conventional means, depending on the nature of the reinforcing fiber material being sized and the type of applicator being used. Such means for adjusting the amount of size pickup include varying the applicator speed, increasing or decreasing the concentration of the sizing composition, increasing or decreasing the viscosity of the sizing by adding viscosity modifiers, or by changing the temperature of the sizing.

For example, where the reinforcing fiber material is a continuous fiber strand, the sizing composition may be applied by contacting the fiber strand with a roller applicator containing the sizing composition. In such a process, the speed of the roller applicator can be varied to change the amount of sizing composition that is applied to the surface of the continuous fiber strand. Accordingly, it is possible to increase or decrease the level of impregnation of the continuous fiber strand with the sizing composition, and, accordingly, the amount of sizing composition present on the surface of the continuous fiber strand, by decreasing or increasing the speed of the roller applicator. The roller applicator speeds that may be used in the process of sizing according to the invention may vary from about 15 rpm to about 120 rpm. Preferably, roller applicator speeds from about 30 rpm to about 75 rpm may be used.

The sized reinforcing fiber material may then be used in continuous form, for example, in the formation of filament wound composites, or as input for a weaving or knitting process to make a fabric. The fabric may subsequently be used in a centrifugal casting process or as input for an RTM or SCRIMP molding process. In a preferred embodiment, the sizing composition is applied to reinforcing fibers used to manufacture filament wound composite articles, such as pipes. In this respect, the sized reinforcing

fibers are impregnated with a catalytically activated cycloolefin resin, and a polymerization reaction allowed to progress until a hardened composite is formed. In another embodiment of the present invention, the sized reinforcing fibers may be laid down as a mat, which is then impregnated with the activated cycloolefin resin to be  
5 polymerized. In yet another embodiment, the sized reinforcing fibers are woven or knitted into a fabric that is then impregnated and molded with the activated cycloolefin resin.

The cycloolefin resin used to form the composite of the present invention includes any suitable cycloolefin that can be polymerized by a ring opening metathesis  
10 polymerization reaction. The term "cycloolefin resin" as it is used herein, is intended to include monomers, dimers, tetramers, pentamers, or oligomers of conventionally known cycloolefin resins. Typically the cycloolefin resin is a liquid resin which is cured or hardened by the ROMP polymerization process. A suitable cycloolefin may be selected from the group consisting of cyclobutene, cyclopentene, cycloheptene, cyclooctene,  
15 cyclooctadiene, cyclopentadiene, dicyclopentadiene, 7-oxanorbornene, 7-oxanorbornadiene, tetracyclododecadiene, cyclododecene, cyclononadiene, cyclopentadiene trimers or tetramers, dicyclopentadiene trimers or tetramers, and mixtures thereof. For example, the cycloolefin resin may be a dicyclopentadiene (DCPD) resin, such as DCPD resins having the tradenames "Ultrene 99" and "Ultrene 97", which may be  
20 obtained commercially from B.F. Goodrich Inc.

The cycloolefin resin may preferably be used in combination with an effective amount of a gel modification agent, which slows the hardening of the cycloolefin resin during the polymerization or curing process and thus allows sufficient time to form and shape the combination of the cycloolefin resin and the reinforcing fiber material. An  
25 exemplary composite molding process that describes using a combination of a cycloolefin resin and a gel modification agent is disclosed in U.S. Patent No. 5,266,370. Any suitable gel modification agent may be used in the composite molding process of the present invention. An example of a suitable gel modification agent is triphenyl phosphine (TPP), which is commercially available, for example, as Product No. T8,440-9, from Aldrich  
30 Chemical Co.

Suitable ROMP catalysts that may be used to form the molded composite articles of this invention may be selected from the group consisting of ruthenium and osmium catalysts. A ROMP catalyst useful in this invention may be selected from the group

consisting of ROMP catalysts described, for example, in U.S. Patent Nos. 5,312,940, 5,342,909, 5,831,108, 5,840,238, 5,849,851 and 5,939,504. Preferably, ROMP catalysts suitable for use with the non-poisoning sizing compositions of this invention are ruthenium catalysts and osmium catalysts including those represented by Formula I:



in which M is selected from ruthenium or osmium; R and R<sup>1</sup> are selected from hydrogen, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl, C<sub>1</sub>-C<sub>20</sub> alkyl, aryl, C<sub>1</sub>-C<sub>20</sub> carboxylate, C<sub>1</sub>-C<sub>20</sub> alkoxy, C<sub>2</sub>-C<sub>20</sub> alkenyloxy, C<sub>2</sub>-C<sub>20</sub> alkynyloxy, aryloxy, C<sub>2</sub>-C<sub>20</sub> alkoxy carbonyl, C<sub>1</sub>-C<sub>20</sub> alkylthio, C<sub>1</sub>-C<sub>20</sub> alkylsulfonyl or C<sub>1</sub>-C<sub>20</sub> alkylsulfinyl; each optionally substituted with C<sub>1</sub>-C<sub>5</sub> alkyl, halogen, C<sub>1</sub>-C<sub>5</sub> alkoxy or with a phenyl group optionally substituted with halogen, C<sub>1</sub>-C<sub>5</sub> alkyl or C<sub>1</sub>-C<sub>5</sub> alkoxy; X and X<sup>1</sup> are selected from any anionic ligand; and L and L<sup>1</sup> are selected from any neutral electron donor. An anionic ligand is defined as any ligand which, when removed from a metal center in its closed shell electron configuration, has a negative charge. A neutral electron donor is any ligand which, when removed from a metal center in its closed shell electron configuration, has a neutral charge, such as a Lewis base. An example of a preferred ROMP catalyst according to the present invention is phenylmethylenebis(tricyclohexylphosphine)ruthenium dichloride, which is commercially available from Advanced Polymer Technologies, Inc.

The ROMP catalyst is used in amount effective to initiate the polymerization of the cycloolefin resin. This effective amount is proportionate to the batch weight of resin being molded. Accordingly, the weight/weight ratio of cycloolefin resin in relation to the ROMP catalyst in the sizing composition may range from about 600:1 to about 1700:1. Preferably, the weight ratio of cycloolefin resin to the ROMP catalyst is approximately 1250:1.

The ROMP catalyst may be dissolved in a solvent before it is combined with the cycloolefin resin for molding. Any suitable solvent may be used to dissolve the ROMP catalyst. Suitable solvents are those that are non-reactive during the polymerization of the activated cycloolefin resin. Examples of suitable solvents include hydrocarbons, toluene, xylene, trichloroethane, methylene chloride and water. A preferred solvent is methylene chloride. Alternatively, the ROMP catalyst may be used without first dissolving it in a solvent.

The process by which a molded composite article is prepared according to the invention can be accomplished by first dissolving a gel modification agent such as

triphenyl phosphine (TPP), in a cycloolefin resin such as DCPD, the cycloolefin resin having been melted by warming to a temperature of from about 90°F to 120°F. Subsequently, the catalyst, dissolved in a solvent such as methylene chloride, may be added to the combination of the cycloolefin resin and the gel modification agent, and the mixture stirred for approximately two minutes.

The resulting resin mixture may then be combined, by any molding means conventionally known in the art, with a reinforcing fiber material sized according to the present invention. Such molding means include, but are not limited to, resin injection molding, centrifugal casting, and filament winding. For example, where the desired composite is a filament-wound composite, strands of the reinforcing fiber material may be pulled through a bath containing the resin mixture, to provide strands impregnated with resin mixture. The impregnated strands may then be wound, for example, on a mandrel, to form a raw composite in the form of a filament wound pipe or ring. This raw composite may be cured by a process including gelling and post-curing according to any method conventionally known in the art. For example, the raw composite may be allowed to gel, preferably at a temperature between 90°F and 140°F. The gelling is caused by the initiation of polymerization of the cycloolefin resin. The gelled composite may then be fully cured by heating in an oven, for example, at about 300°F for from 1 to 16 hours. After the cure is completed, the composite may be allowed to cool, and then removed from the mandrel. In this manner, an effective ROMP polymerization process using the sized reinforcing fiber material and the combination of a ROMP catalyst and cycloolefin resin according to the present invention can provide a tough, resilient composite. Additionally, as mentioned previously, the sized reinforcing fiber material may also be successfully molded by any other conventional molding means known in the manufacture of fiber-reinforced composites.

The sized reinforcing fiber materials of the present invention include strands, rovings, yarns or threads, in continuous or chopped form, fibrous fabrics, mats and surfacing veils. The term "strand" as used herein, is intended to include a collection of a plurality of individual filaments, typically from about 20-8000 filaments, and preferably from about 2000-4000 filaments. Any suitable reinforcing fiber material may be used in the molded composite article of the present invention. The reinforcing fiber material may be made from any suitable molten fiberizable material, or from any fibrous material. Preferably, the reinforcing fiber material is selected from the group consisting of glass,

carbon, graphite, aramid (such as Kevlar®) or other polymer fibers, such as Spectra®, natural fibers, or blends thereof, as well as any other fibrous reinforcing materials that may conventionally be used in the manufacture of reinforced composites.

5 These reinforcing fiber materials, when coated with the sizing composition of the present invention and combined with a catalyzed cycloolefin resin, may be molded into composite articles by any molding procedure conventionally known in the art. The composite articles of the present invention may include filament wound composites such as pipes, fittings, shafts or waterfront or ocean pilings; or composite articles formed by resin injection molding (RIM), such as automobile parts, recreational vehicle parts, or  
10 chemical process equipment. Other composite articles within the scope of the present invention may be formed by centrifugally casting the cycloolefin resin, catalyst and a woven or knitted fabric or mat made according to the invention described in U.S. Patent No. 5,266,370.

15 The following examples are representative, but are in no way limiting as to the scope of this invention.

## EXAMPLES

### Example 1

20 An exemplary sizing composition was prepared according to the following composition:

Vinyltrimethoxysilane	0.300% by weight
Glacial acetic acid	0.090% by weight
Polyurethane dispersion	5.300% by weight
Cationic lubricant	0.100% by weight
25 Balance	Water

The vinyltrimethoxysilane was first dissolved in water and glacial acetic acid added as a hydrolyzing agent to facilitate dissolution and hydrolysis. The cationic lubricant, which is water-soluble, and the polyurethane dispersion, in water, were then added to the silane solution to form an aqueous solution or dispersion. The resulting solution, that is, the  
30 sizing composition, was then applied to glass roving ends using a rotating applicator and dried in an oven for 13 to 25 hours at 265°F.

Example 2

Various sizing compositions according to the present invention, as shown in Table 1 below, were prepared. The percentage weight or the amount by weight of each component necessary to make a 50,000 gram batch is indicated, the balance being

5 comprised of water as the solvent.

Table 1

Material	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8
	% weight composition							
W320 Suspension <sup>a</sup>	4.696	3.196	3.100	4.600	3.996	2.496	2.400	3.900
A-171 <sup>b</sup>	0.100	0.100	0.100	0.100	0.800	0.800	0.800	0.800
Acetic Acid	0.360	0.360	0.360	0.360	0.360	0.360	0.360	0.360
Henkel 2658 <sup>c</sup>	0	1.500	1.500	0	0	1.500	1.500	0
Henkel 6760T <sup>d</sup>	0.004	0.004	0.100	0.100	0.004	0.004	0.100	0.100
Fiberglass X-12 <sup>e</sup>	0	0	0	0	0	0	0	0
SM2154 <sup>f</sup>								
% Total Solids	4.800	4.800	4.800	4.800	4.800	4.800	4.800	4.800
50,000 gm mix	Weight (g)							
W320 Suspension <sup>a</sup>	7826.7	5326.7	5166.7	7666.7	6660.0	4160.0	4000.0	6500.0
A-171 <sup>b</sup>	94.3	94.3	94.3	94.3	754.7	754.7	754.7	754.7
Acetic Acid	720.0	720.0	720.0	720.0	720.0	720.0	720.0	720.0
Henkel 2658 <sup>c</sup>		750.0	750.0			750.0	75.0	
Henkel 6760T <sup>d</sup>	16.0	16.0	400.0	400.0	16.0	16.0	400.0	400.0
Fiberglass X-12 <sup>e</sup>								
SM2154 <sup>f</sup>								
Fuzz (g/100 yd)	.022	.015	.007	.018	.086	.069	.059	.029
Delta L	.45	.65	1.29	.26	.55	1.08	.81	.52
Loss on Ignition (LOI)	.71	.62	.62	.68	.62	.53	.57	.63

<sup>a</sup> W320 - film-forming polyurethane emulsion, Witco Chemical Co.

<sup>b</sup> A-171 - vinyltrimethoxysilane, OSi-Witco Chemical Co.

<sup>c</sup> Henkel 2658 - nonionic lubricant

<sup>d</sup> Henkel 6760T- cationic lubricant

<sup>e</sup> Fiberglass X-12 - emulsified paraffin wax, Michelman, Inc.

<sup>f</sup> SM2154 - silicon lubricant, GE



Table 1 (cont'd)

Material	Ex.9	Ex.10	Ex. 11	Ex. 12	Ex.13	Ex.14	Ex.15	Ex.16
	% weight composition							
W320 Suspension <sup>a</sup>	3.500	3.650	3.650	5.596	4.000	5.000	5.050	5.100
A-171 <sup>b</sup>	0.600	0.450	0.450	0.100	0.100	0.500	0.500	0.500
Acetic Acid	0.360	0.360	0.360	0.360	0.360	0.360	0.360	0.360
Henkel 2658 <sup>c</sup>	0.650	0.650	0.650	0	1.500	0	0	0
Henkel 6760T <sup>d</sup>	0.050	0.050	0.050	0.004	0.100	0.200	0.150	0.100
Fiberglass X-12 <sup>e</sup>	0	0	0	0	0	0	0	0
SM2154 <sup>f</sup>								
% Total Solids	4.800	4.800	4.800	5.700	5.700	5.700	5.700	5.700
50,000 gm mix	Weight (g)							
W320 Suspension <sup>a</sup>	5833.3	6083.3	6083.3	7895.0	5643.3	7054.2	7124.7	7195.3
A-171 <sup>b</sup>	566.0	424.5	424.5	94.3	94.3	471.7	471.7	471.7
Acetic Acid	720.0	720.0	720.0	720.0	720.0	720.0	720.0	720.0
Henkel 2658 <sup>c</sup>	325.0	325.0	325.0		750.0			
Henkel 6760T <sup>d</sup>	200.0	200.0	200.0	16.0	400.0	800.0	600.0	400.0
Fiberglass X-12 <sup>e</sup>								
SM2154 <sup>f</sup>								
Fuzz (g/100 yd)	.043	.021	.056	.013	.002	.009	.014	.027
Delta L	1.00	1.20	.98	.50	1.36	.77	.55	.58
Loss on Ignition (LOI)	.59	.64	.75	.69	.62	.63	.65	.64

Table 1 (cont'd)

Material	Ex.17	Ex.18	Ex.19
	% weight composition		
W320 Suspension <sup>a</sup>	4.600	2.300	2.200
A-171 <sup>b</sup>	0.500	0.500	0.800
Acetic Acid	0.360	0.360	0.140
Henkel 2658 <sup>c</sup>	0.500	0.500	0
Henkel 6760T <sup>d</sup>	0.100	0.100	0
Fiberglass X-12 <sup>e</sup>	0	2.300	0
SM2154 <sup>f</sup>		0	0.500
% Total Solids	5.700	5.700	3.500
50,000 gm mix	Weight (g)		
W320 Suspension <sup>a</sup>	6489.8	3244.9	6166.7
A-171 <sup>b</sup>	471.7	471.7	754.7
Acetic Acid	720.0	720.0	72.0
Henkel 2658 <sup>c</sup>	250.0	250.0	0
Henkel 6760T <sup>d</sup>	400.0	400.0	0
Fiberglass X-12 <sup>e</sup>		2875.0	0
SM2154 <sup>f</sup>			458.7
Fuzz (g/100 yd)	.015	.006	.046
Delta L	.95	.58	.20
Loss on Ignition (LOI)	.60	.59	.52

It was observed from these results that addition of a nonionic lubricant such as PEG 400 monopelargonate as a processing aid contributed to growth in the forming package. This growth was measured as the change in doff length of the forming package after drying and winding the sized reinforcing fiber material, and reported as delta L.

- 5 Adding the silicon lubricant was not as effective as adding a cationic lubricant in the sized fiber product. A high level of fuzz was also observed when a higher level of silane coupling agent was used. Consequently, it was concluded that while the silane coupling agent, lubricant and processing aid are desirably added to the sizing composition of the present invention, it is necessary to balance the proportions of each of these components
- 10 to avoid compromising product quality.

### Example 3

- Fiber reinforcing materials in the form of continuous glass fiber strands were treated with each of the sizing compositions of Examples 12-19, at applicator rotation
- 15 speeds that were varied to change the amount of sizing composition deposited on the surfaces of the glass fiber strands. Eight samples of glass fiber strand that had been sized with the sizing composition of each of Examples 12-19 were prepared and tested at each applicator speed. The glass fiber strand samples were sized at applicator rotation speeds of 45 rpm and 75 rpm, respectively. The resulting sized glass fiber strands were evaluated

for the development of fuzz, package growth measured as delta L, and loss on ignition rate. The average test values for each group of eight samples is reported in Table 2.

Table 2

Sizing Composition	45 rpm applicator speed			75 rpm applicator speed		
	Delta L	Fuzz	LOI (%)	Delta L	Fuzz	LOI (%)
Ex. 12	0.50	0.0129	0.69	0.45	0.229	0.90
Ex. 13	1.36	0.0018	0.62	1.00	0.0066	0.87
Ex. 14	0.77	0.0082	0.63	0.45	0.0094	0.85
Ex. 15	0.55	0.0142	0.65	N/A	N/A	N/A
Ex. 16	0.58	0.0268	0.64	N/A	N/A	N/A
Ex. 17	0.95	0.0148	0.60	0.70	0.0099	0.82
Ex. 18	0.58	0.0059	0.59	0.65	0.0080	0.70
Ex. 19	0.20	0.0460	0.52	0.20	0.0463	0.52

- 5 The results indicated that the glass fiber strands sized according to the invention exhibited low fuzz. A preferred composition of the present invention, which included a film forming polymer, a silane coupling agent, a cationic lubricant, a nonionic lubricant and an emulsified paraffin wax, as taught in Example 18, exhibited very low fuzz, about 0.0059 at an application rate of 45 rpm (0.0080 at 75 rpm), and low LOI (0.59 at 45 rpm and 0.70 at 75 rpm, respectively).

#### Example 4

- 15 Samples of glass rovings that had been sized with the sizing compositions of Examples 12-19 were also evaluated for resin compatibility with DCPD cycloolefin resin, using a dry and a wet interlaminar shear test, as described in ASTM Standard Method No. 2344. The wet shear test was performed after boiling a DCPD composite made with the sized rovings in water for 72 hours. As reported in Table 3, the results include the % strength retention of the sample, which corresponds to the difference between the dry shear and wet shear values.

Table 3

	Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex. 16	Ex. 17	Ex. 18	Ex. 19
Dry Shear	1332	1338	2325	2340	2475	2271	1946	2630
Wet Shear	435	808	1734	1797	1966	1474	1417	2193
Dry SD	141	120	196	194	164	111	204	178
Wet SD	70	135	137	119	155	122	127	157
% Retention	33	60	72	77	83	80	73	84
% Glass std.	81	80	81	82	80	80	76	77

SD: standard deviation, 95% confidence limit

% Glass std: glass content as percentage weight

An examination of the wet strength retention of these composite samples indicates that increasing the amount of silane has the effect of improving the percentage strength retention. The higher strength retention is an indicator of improved adhesion between the surface of the glass roving and the cycloolefin resin.

5

#### Example 5

A continuous strand of glass fiber roving that had been sized according to the invention were used to prepare a filament wound composite by molding the sized roving with a DCPD resin. 1000 grams of a DCPD monomer were liquefied by warming to a  
10 temperature of about 94°F. 0.83 grams of triphenyl phosphine (TPP, Product No. T8,440-9, Aldrich Chemicals) were dissolved in the liquefied DCPD resin. Subsequently, 0.80 grams of a ROMP catalyst, phenylmethylenebis(tricyclohexylphosphine) ruthenium dichloride, were dissolved in 1.0 grams methylene chloride and added to the mixture of DCPD and TPP, and the resulting  
15 mixture stirred for approximately 2 minutes. This final mixture of the monomer, catalyst and inhibitor was then poured into a resin bath. The glass fiber roving was then pulled through the resin bath and was thus impregnated with the resin mixture. The impregnated roving was then wound on a mandrel to form a raw composite in the shape of a filament wound pipe or ring. The raw composite was allowed to gel at room temperature, and then  
20 fully cured by placing the gelled composite in an oven at 300°F, for 1 to 16 hours. The cured composite was then allowed to cool and removed from the mandrel. It is believed that Applicants' invention includes many other embodiments which are not herein specifically described, accordingly this disclosure should not be read as being limited to the foregoing examples or preferred embodiments.

## WHAT IS CLAIMED IS:

1. A sizing composition compatible with a ROMP catalyst used to initiate a ring opening metathesis polymerization reaction of a cycloolefin resin, comprising:
  - one or more film forming polymers;
  - 5 a silane coupling agent; and
  - a lubricant;wherein the film forming polymer, the silane coupling agent and the lubricant are compatible with the ROMP catalysts used to initiate ring opening metathesis polymerization of cycloolefin resins.
- 10 2. The sizing composition of claim 1, further comprising an emulsified paraffin wax.
3. The sizing composition of claim 1, wherein the film forming polymer is a polyurethane.
4. The sizing composition of claim 1, wherein the silane coupling agent is  
15 selected from the group consisting of vinyltrimethoxysilane, vinyltriethoxysilane, phenylaminosilane, methacryloxypropyltriethoxysilane, n-2-(vinylbenzylaminoo)-ethyl-3-aminopropyltrimethoxysilane-monohydrogen chloride, and gamma aminopropyltriethoxysilane.
5. The sizing composition of claim 4, wherein the silane coupling agent is  
20 vinyltrimethoxysilane.
6. The sizing composition of claim 1, wherein the lubricant is a cationic lubricant.
7. The sizing composition of claim 6, wherein the cationic lubricant is a functionalized polyalkyleneimine.
- 25 8. The sizing composition of claim 7 wherein the cationic lubricant is a partially amidated polyethyleneimine.
9. The sizing composition of claim 1, further comprising a hydrolyzing agent.
10. The sizing composition of claim 9, wherein the hydrolyzing agent is selected from the group consisting of hydrochloric, acetic, formic, citric, oxalic and  
30 phosphorous acids.
11. The sizing composition of claim 10, wherein the hydrolyzing agent is glacial acetic acid.

12. The sizing composition of claim 1, further comprising one or more additives selected from the group consisting of wetting agents and processing aids.
13. The sizing composition of claim 12, wherein the processing aid is a salt free PEG 400 monopelargonate.
- 5 14. A sizing composition compatible with a ROMP catalyst used to initiate a ring opening metathesis polymerization of a dicyclopentadiene resin, comprising:  
a polyurethane film forming polymer compatible with the ROMP catalyst;  
a silane coupling agent selected from the group consisting of  
vinyltrimethoxysilane, vinyltriethoxysilane, phenylaminosilane,  
10 methacryloxypropyltriethoxysilane, n-2-(vinylbenzylaminoo)-ethyl-3-aminopropyltrimethoxysilane-monohydrogen chloride, and gamma aminopropyltriethoxysilane;  
an emulsified paraffin wax; and  
a partially amidated polyalkyleneimine.
- 15 15. A sized reinforcing fiber material comprising a reinforcing fiber material coated with a sizing composition comprising:  
one or more film forming polymers; a silane coupling agent; and  
a lubricant;  
wherein the film forming polymer, the lubricant and the silane coupling agent are  
20 compatible with ROMP catalysts used to initiate ring opening metathesis polymerization of cycloolefin resins.
16. The sized reinforcing fiber material of claim 15, wherein the reinforcing fiber material comprises one or more fibers selected from the group consisting of glass, aramid, other polymer fibers, natural fibers, and blends thereof.
- 25 17. The sized reinforcing fiber material of claim 15, wherein the film forming polymer in the sizing composition is a polyurethane.
18. The sized reinforcing fiber material of claim 15, wherein the silane coupling agent in the sizing composition is selected from the group consisting of  
vinyltrimethoxysilane, vinyltriethoxysilane, phenylaminosilane,  
30 methacryloxypropyltriethoxysilane, n-2-(vinylbenzylaminoo)-ethyl-3-aminopropyltrimethoxysilane-monohydrogen chloride, and gamma aminopropyltriethoxysilane.

19. The sized reinforcing fiber material of claim 15, which is in the form of a yarn, a thread, a fibrous fabric, or a mat.
20. A composite article comprising:
- 5 i) a reinforcing fiber material sized with a sizing composition comprising:
- one or more film forming polymers;
- a silane coupling agent; and
- a lubricant;
- wherein the film forming polymer, the lubricant and the silane coupling
- 10 agent are compatible with ROMP catalysts used to initiate ring opening metathesis polymerization of cycloolefin resins; and
- ii) a cycloolefin resin that is catalytically cured using a ring opening metathesis polymerization reaction.
21. The composite article of claim 20, wherein the film forming polymer in the
- 15 sizing composition is a polyurethane.
22. The composite article of claim 20, wherein the silane coupling agent in the sizing composition is selected from the group consisting of vinyltrimethoxysilane, vinyltriethoxysilane, phenylaminosilane, methacryloxypropyltriethoxysilane, n-2-(vinylbenzylaminoo)-ethyl-3-aminopropyltrimethoxysilane-monohydrogen chloride, and
- 20 gamma aminopropyltriethoxysilane.
23. The composite article of claim 20, wherein the cycloolefin resin is dicyclopentadiene.
24. The composite article of claim 20, wherein the reinforcing fiber material comprises one or more fibers selected from the group consisting of glass fibers, polymer
- 25 fibers, carbon or graphite fibers, natural fibers and combinations thereof.
25. The composite article of claim 20, wherein the film forming polymer in the sizing composition is a polyurethane.
26. A composite article formed by a process comprising:
- 30 i) sizing a reinforcing fiber material with a sizing composition comprising a film forming polymer, a silane coupling agent and a lubricant; wherein the film forming polymer, the silane coupling agent and the lubricant are compatible with ROMP catalysts used to initiate ring opening metathesis polymerization of cycloolefin resins;

ii) impregnating the reinforcing fiber material sized with a catalyzed resin, which has been prepared by adding a catalytically effective amount of a ROMP catalyst to a cycloolefin resin to form the catalyzed resin; and

iii) allowing the catalyzed resin to polymerize to form the fiber reinforced composite.

27. A method of making a fiber reinforced composite comprising the steps of:

i) applying a sizing composition on the surfaces of a reinforcing fiber material, the sizing composition comprising:

one or more film forming polymers;

a silane coupling agent; and

a lubricant;

to form a coated fiber reinforcing material; and

ii) molding the coated fiber reinforcing material with a cycloolefin resin in the presence of a ROMP catalyst to form a fiber reinforced composite;

wherein the film forming polymer, the silane coupling agent and the lubricant in the sizing composition are compatible with one or more ROMP catalysts used to initiate ring opening metathesis polymerization of the cycloolefin resins.

28. A method of making a sized reinforcing fiber material comprising the steps of:

i) preparing a sizing composition according to claim 1; and

ii) contacting the surfaces of a plurality of filaments of a reinforcing fiber material with the sizing composition; and

iii) allowing the sizing composition to solidify on the surfaces of the filaments of reinforcing fiber material.

29. The method of claim 28, wherein the step of applying the sizing composition on the surfaces of a reinforcing fiber material comprises drawing the reinforcing fiber material through a bath including a roller applicator covered with the sizing composition.

30. The method of claim 29, wherein the step of drawing the reinforcing fiber material through the bath including a roller applicator covered with the sizing composition is performed at an applicator speed of from about 30 rpm to about 75 rpm.



31. The method of claim 28, wherein the step of applying the sizing composition is accomplished using sprayers, pads, rollers, sizing dies or immersion baths, or any combination thereof.

## INTERNATIONAL SEARCH REPORT

Intern: Application No

PCT/US 01/00476

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C03C25/26 C03C25/32 C08J5/06 C08K7/02 C08G61/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C03C C08J C08K C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 271 229 A (TEMPLE CHESTER S) 2 June 1981 (1981-06-02) column 4, line 46 - column 5, line 37 column 6, line 42 - line 54 table I claims	1-19, 28-31
Y	---	20-27
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Y	---	20-27
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents:

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## INTERNATIONAL SEARCH REPORT

Intern Application No

PCT/US 01/00476

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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